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## **HIGH ENERGY CRYSTALLINE LASER MATERIALS**

**Semiannual Technical Summary Report**  
**16 April 1966 to 16 October 1966**

**18 November 1966**

**Contract Nonr-4850(00)**  
**ARPA Order No. 596**  
**Code No. 4730**

**Expiration Date March 31, 1967**

**R. C. Ohlmann, Principal Investigator**  
**R. Mazelsky**  
**J. Murphy**

**R. D. Haun, Jr., Manager, Quantum Electronics R&D**



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# **HIGH ENERGY CRYSTALLINE LASER MATERIALS**

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# ABSTRACT

The spectroscopic study of  $\text{GdAlO}_3$  doped with  $\text{Cr}^{3+}$  between 2° and 300°K revealed a structure to the "R" lines which is described by a ferromagnetic exchange interaction with the  $\text{Gd}^{3+}$  ions, with  $J = 2.1 \text{ cm}^{-1}$  for the ground state and  $J = 3.2 \text{ cm}^{-1}$  for the excited state of  $\text{Cr}^{3+}$ . The selection rules on the transitions are qualitatively discussed in order to explain the change in the fluorescence spectrum between 2 and 4°K. The fluorescence lifetime is 9.0, 15.4, and 18.0 ms at 2.0, 4.2, and 77°K respectively.

## INTRODUCTION

The object of this contract is to study potential crystalline laser materials with the ultimate aim of obtaining improved materials for high energy lasers. The studies primarily consist of fluorescence and absorption spectroscopy and crystal growth investigations.

One material that has proved worth studying and has laser potentiality is chromium-doped gadolinium aluminum perovskite,  $\text{GdAlO}_3\text{:Cr}$ . This material has been considered as a Q-spoiled laser because it may have six times the energy storage capability per unit volume as ruby (with 0.05% Cr). This possible improvement should occur because six times as large a chromium ion concentration can be used in  $\text{GdAlO}_3$  as compared to  $\text{Al}_2\text{O}_3$  without causing either a quenching of the R-line fluorescence or excessive gain or excessive absorption of the pump light. However, crystal growth technology has to be developed for  $\text{GdAlO}_3$  crystals to have them approach the quality of ruby crystals.

From a basic physics viewpoint,  $\text{GdAlO}_3\text{:Cr}$  shows the interesting characteristic of having the sharp-lines in the absorption and emission spectra of  $\text{Cr}^{3+}$  modified significantly by the presence of a ferromagnetic exchange interaction between each chromium ion and the eight  $\text{Gd}^{3+}$  ions surrounding it. We have attempted to describe the experimental results by means of an isotropic exchange interaction and have had moderate success in fitting the shape of the fluorescence spectrum at 4.2°K. However, the change of the spectrum observed between 4.2° and 2.2°K required a consideration of the selection rules and possible perturbations on our simple model.

The experimental results and some of the theoretical thinking is presented in the appendix,<sup>1</sup> which is a reprint of a paper presented

at the conference on the "Optical Properties of Ions in Crystals" held at Johns Hopkins University on 12 September 1966. The details of the theoretical approach for the simple model was given in the Final Technical Summary Report<sup>2</sup> on the present contract, dated 15 November 1965.

From an applied physics viewpoint, the study of the causes of the line shape is important in determining if the 50A line width is "homogeneously" broadened in the sense that all ions are equivalent and whether all the ions will participate in the amplification of a narrow bandwidth electromagnetic wave. We believe the ions are practically equivalent but whether they can be stimulated to emit in a single pulse depends on the relaxation time of the ions in the exchange-split excited (<sup>2</sup>E) state, a quantity that can be measured after laser action is attained.

The crystal growth effort on gadolinium aluminum oxide has been minimal in the last six months due to unexpected delays in obtaining iridium crucibles and in setting up a growth station to pull crystals from the melt. Since the crucibles have recently been delivered and the crystal pulling apparatus is almost complete crystals will be grown in the near future.

Since much of the work on this contract during the last period is described in the paper included as an appendix, the body of this report consists of a review of earlier work, an abstract of the scientific paper, and an outline of the direction the work will take in the next period.

## PROPERTIES OF $\text{Cr}^{3+}$ IN $\text{GdAlO}_3$

### Experimental

The fluorescence spectra of powders and a crystal of  $\text{GdAl}_{1-x}\text{Cr}_x\text{O}_3$  have been obtained at a number of temperatures between 2.2°K and 300°K for values of  $x$  from 0.0005 to 0.005 (estimated  $x$  for the crystal was 0.002). The emission of chromium ions even at 0.5% concentration came primarily from ions unaffected by other nearby chromium ions. From the x-ray data of Geller and Bala,<sup>3</sup> 0.5% of the aluminum sites is equivalent to  $9.65 \times 10^{19}$  Cr ions/cm<sup>3</sup>.

The fluorescence spectrum at 300°K consists of a 50Å wide line peaking at 7275Å along with a low intensity background between 6800 and 7800Å. At 77°K the background on the short wavelength side of the line disappears and the broad line shows structure indicating five partially resolved lines estimated to be at 7238, 7245, 7263, 7274, and 7288Å. At 4.2°K the 7238Å line disappears and the remaining lines become somewhat better resolved (see Fig. 1 of the appendix). As the temperature is further reduced to 2.15°K the 7288Å line decreases in intensity and the separation of the other three lines decreases, their peaks occurring at about 7254, 7261, and 7269Å (see Fig. 2 of the appendix). The theory described in the next section is an attempt to explain these characteristics of the fluorescence spectra.

Two other features of the fluorescence spectra will be described here although they have not been considered in detail. Two partially resolved lines appear at 4.2°K and 0.2% and 0.5% concentration which are believed to be due to pairs of chromium ions. They are located at 7351 and 7348Å, which, on an energy scale, averages  $160 \text{ cm}^{-1}$  from the center of the main lines. The other characteristic is the positions of the vibrational side bands -- these consist of broad peaks even at 2.2°K, with centers about 270, 440, 620 and  $750 \text{ cm}^{-1}$  away from the main lines.



Intimately related to the fluorescence spectra is the decay time of the emission lines after a short excitation pulse. In the orthorhombic distortion of the cubic perovskite, space-group  $D_{2h}^{16}$ , to which  $GdAlO_3$  belongs,<sup>3</sup> the aluminum sites have only inversion symmetry and, in general, there are two types of aluminum sites which are inequivalent. Since the distortion is small in  $GdAlO_3$  these sites are probably almost equivalent and their difference may not be observable. To ascertain whether the structure observed in the fluorescence spectrum arises from  $Cr^{3+}$  on inequivalent aluminum sites, the decay time was observed at 2.2° and 4.2°K for each of the spectrally selected lines in the fluorescence spectrum. The decay time of each of the lines was found to be the same within a 3% uncertainty. This equality is a necessary though not sufficient condition for the Cr ions to be equivalent. Table I lists the decay time measured at several temperatures.

Table I

Temperature (°K)	Decay Time (ms)
2.0	9.0
4.2	15.4
77	18.0
300	13.0

No lag in the rise of the fluorescence after the pulse excitation was observed greater than 0.2 ms, the minimum detectable time, indicating any thermal relaxation bottlenecks must be at least that fast. The decay times listed in Table I are not believed to be influenced by radiation trapping since the absorption strength is very weak and its spectrum only slightly overlaps the emission spectrum, as described below.

The excitation spectrum of the fluorescence lines and the absorption spectrum of the single crystal have been measured for sample temperatures between 2.2°K and 300°K. The corrected excitation spectrum is very similar to the absorption spectrum for wavelengths less than 7200Å. The general features, which have been reported earlier,<sup>2</sup> consist of two broad bands in the visible peaking at 5600 and 4150Å, strong lines in the ultraviolet below 3140Å due to Gd<sup>3+</sup> absorption which is effective in exciting Cr<sup>3+</sup> fluorescence and weak lines at 6910 and 6955Å due to absorption into the <sup>2</sup>T<sub>1</sub> excited state.

Of greater direct interest in investigating the Cr-Gd interactions is the absorption in the region of the main emission lines. This was relatively difficult to measure in the crystal we had available since the total absorption at the peak of the absorption lines was about 0.5%, i.e., a transmission of 99.5%, at room temperature, increasing to a few percent in liquid helium. The integrated absorption cross section increased almost an order-of-magnitude as temperature was reduced from room temperature to 2.2°K. The absorption spectrum observed at 2.2°K, shown Fig. 3 of the appendix, consists of two 8Å-wide lines at 7226 and 7241.5Å. The shape of these lines and their shift from the positions of the fluorescence lines are also subjects treated by the theoretical model.

We have also calculated the integrated absorption coefficient,  $\int \sigma d\bar{\nu}$ , of both "R" lines.\* The uncertainties resulting from poor crystal quality and the use of converging unpolarized light allows only an estimate of  $\int \sigma d\bar{\nu} = 10^{-19}$  cm within a factor of two. Using the relationship between decay time and integrated absorption coefficient given by<sup>4</sup>

$$\tau^{-1} = 16 \pi n^2 \bar{\nu}^2 c \int \sigma d\bar{\nu} \quad (1)$$

\* In these equations  $\bar{\nu}$  is the frequency in cm<sup>-1</sup>,  $\sigma$  is the absorption cross section in cm<sup>2</sup>, and  $n$  is the index of refraction estimated to be 2.3.

we calculate a decay time of about 7 ms, remarkably close to the observed value considering the theoretical and experimental approximations made.

### Theoretical

In order to explain the experimental line shapes in the region of the "R" lines of  $\text{Cr}^{3+}$  we started with the simple model of an isotropic Heisenberg exchange interaction between each chromium ion and the eight gadolinium ions surrounding it, and further assumed an equal interaction strength with each of the gadolinium ions.<sup>2</sup> The Hamiltonian is of the form,  $-J S_{\text{Cr}} \cdot \sum S_{\text{Gd}}$ . The energies of this interaction (in units of J) were calculated for both the ground states and first excited electronic states of  $\text{Cr}^{3+}$  ( ${}^4\text{A}_2$  and  ${}^2\text{E}$  respectively) coupling to the  ${}^8\text{S}_{7/2}$  ground states of each  $\text{Gd}^{3+}$  ion. This was done in terms of the total spin quantum numbers,  $S = \sum S_{\text{Gd}}$  between 0 and 28,  $S_{\text{Cr}} = 3/2$  for the  ${}^4\text{A}_2$  and  $1/2$  for the  ${}^2\text{E}$  state, and  $\underline{S} = S_{\text{Cr}} + S$  between  $1/2$  and  $29\ 1/2$  for the ground state. The degeneracy of each of these exchange-split levels was then calculated (see Fig. 4 of the appendix) which then determined the density of states. The fluorescence spectrum at  $4.2^\circ\text{K}$  was compared to the density of the ground states and the agreement was relatively good after fitting the curves by adjusting the value of J to be  $2.1\text{ cm}^{-1}$  (see Fig. 5 of the appendix).

By the same process the absorption spectrum at  $2.2^\circ\text{K}$  can be fit to the density of the excited states, although now a value of J of  $3.2\text{ cm}^{-1}$  is required to fit the peak separation. Figure 6 in the appendix shows the energies and degeneracies of both the ground and excited exchange-split levels. The similarity of the results of our model and the spectra suggests a degree of validity of the model, although a number of questions arose as we studied the problem in greater depth.

The problems that arise are primarily connected with a determination of the selection rules for the transitions. Assuming that the Cr-Gd system comes into thermal equilibrium with the lattice, a perfect agreement between the fluorescence spectrum and the density of

ground states would imply equal matrix elements between the lowest excited state and each of the ground states. That appears unreasonable since it would mean that large changes in the spin quantum numbers in the transition are as probable as small changes.

We also note that the change in shape of the fluorescence spectrum as temperature is reduced to 2.2°K reduces the match between the density of states and the spectrum from that at 4.2°K. This fact is a clue to a qualitative understanding of the selection rules governing these transitions. A calculation of the exact selection rules has not been attempted because the large number of states involved would require a computer calculations, and, even more important, because the perturbations due to unequal values of  $J$  for the interaction with different gadolinium ions, the presence of anisotropic exchange, the interaction with next-nearest neighbors, and the presence of Gd-Gd interactions cannot be calculated quantitatively at present.

Without any of the perturbations being present we would expect that the total spin,  $S$ , of the gadolinium cluster is conserved in the transition. Therefore, at very low temperatures the fluorescence spectra should consist of four sharp lines, with the long wavelength line being considerably weaker due to the selection rules on the  $\text{Cr}^{3+}$  spins. Note that the fluorescence spectrum does show a reduction in the intensity of the long wavelength line as temperature is reduced to 2.2°K. The observed spectrum however is not sharp, and since inhomogeneous broadening of  $15 \text{ cm}^{-1}$  is not to be expected there must be a breakdown of the selection rules.

The presence of Gd-Gd interactions would allow the selection rules on the total spin of the eight gadolinium ions to be relaxed since it will no longer be a good quantum number. That is, each gadolinium ion near a chromium ion interacts not only with the chromium ion but with six other gadolinium ions, three of which are not on the original cluster. Burns<sup>5</sup> has said that  $\text{GdAlO}_3$  orders antiferromagnetically at about 4°K. Although the Gd-Gd exchange constant required for that ordering temperature is only about  $0.1 \text{ cm}^{-1}$ , or 1/20 of the Gd-Cr exchange constant, the interaction is certainly strong enough to affect the spectrum.

It is useful to note that the exchange splitting of the ground state may make it possible to obtain laser action using  $\text{GdAlO}_3\text{:Cr}$  as a "four-level" system at low temperatures. The strongest peak is about  $83 \text{ cm}^{-1}$  above the ground state, so that at  $77^\circ\text{K}$  ( $kT = 53.5 \text{ cm}^{-1}$ ) its thermal population is  $[Z(\infty)/Z(77^\circ)] \exp(-83/53.5) = 0.21 [Z(\infty)/Z(77^\circ)]$  of what it is at high temperatures, where  $Z$  is the partition function. This effect needs to be studied in more detail taking into account the degeneracies of the upper and lower states. However, it appears logical to defer such a study until after laser action is achieved.

#### FUTURE WORK

The effort to grow optical quality  $\text{GdAlO}_3$  crystals will be increased now that the indium crucibles have been delivered and a new growth station is in operation. Since we already have had some success in growing this compound, the major problem remaining is in obtaining large crystals of good quality while simultaneously having it doped with chromium. It will be necessary to repeat the measurements of the absorption spectrum since our present data on absorption strengths may be as much as 30% in error because of the poor quality of the crystals studied. In addition, some polarization effects may become evident in both the fluorescence and absorption spectra when crystal quality improves.

The study of Gd-Cr interactions may be further extended in perovskite host crystals by double-doping  $\text{LaAlO}_3$  with chromium and gadolinium. By maintaining a low chromium concentration ( $< 0.1\%$ ) and varying the gadolinium concentration (up to 10%) while observing changes in the fluorescence spectra, it should be possible to isolate the spectral features due to simple pairs of Cr-Gd ions. The exchange interaction effect on the spectra should reveal whether the value of  $J$  deduced from our present theory in  $\text{GdAlO}_3$  is maintained for a single pair.

A survey of several other related perovskite crystals doped with chromium and rare-earth ions will also be conducted to compare their characteristics with  $\text{LaAlO}_3$  and  $\text{GdAlO}_3$ . If good crystal quality can be achieved for crystals of rare-earth aluminum perovskites it may be feasible to obtain sufficient energy transfer to rare-earth ions to obtain laser oscillations when these crystals are doped with an impurity rare-earth ion.

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## APPENDIX

### SPECTRUM OF $\text{Cr}^{3+}$ IN $\text{GdAlO}_3$

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#### ABSTRACT

The emission and absorption spectra of the "R lines" of  $\text{Cr}^{3+}$  in  $\text{GdAlO}_3$  are shown to consist of overlapping bands with peak separations in emission of about  $20 \text{ cm}^{-1}$  and in absorption, about  $30 \text{ cm}^{-1}$ . The energy levels of the system derived on the assumption of an isotropic exchange coupling between the  $\text{Cr}^{3+}$  impurity and its nearest neighbor gadolinium ions are found to be capable of describing the principle features of the spectra. The exchange coupling appears to be ferromagnetic with values of the exchange parameters for the  $^4A_2$  and the  $^2E$  states of chromium of  $2.1 \text{ cm}^{-1}$  and  $3.2 \text{ cm}^{-1}$  respectively. The selection rules for the optical transitions are somewhat nebulous, however, there is evidence for a  $\Delta m_s = 0, \pm 1$  selection rule on the chromium matrix elements.



## SPECTRUM OF $\text{Cr}^{3+}$ IN $\text{GdAlO}_3^*$

by

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In  $\text{GdAlO}_3$ , the so-called R lines in the low temperature absorption and fluorescence spectra of  $\text{Cr}^{3+}$  are not sharp lines as in  $\text{LaAlO}_3$ ,<sup>1</sup> a related diamagnetic perovskite, but consist rather of two and four overlapping bands respectively about  $10\text{-}15\text{ cm}^{-1}$  wide.<sup>2</sup>

It is not surprising that the spectra in this material should differ from that found in diamagnetic materials because of the additional perturbations on the  $\text{Cr}^{3+}$  ion arising from exchange effects with the neighboring  $\text{Gd}^{3+}$  ions.

Our understanding of the spectrum is not yet complete. There are, however, certain features of a simple model based upon an isotropic exchange interaction of the  $\text{Cr}^{3+}$  ion with its eight nearest neighbor  $\text{Gd}^{3+}$  ions that shed some light upon the shape of the spectrum and its temperature dependence.

In this paper the quantitative predictions of the simple model are compared with the experimental results. It is found that the selection rules derived from the model appear to be violated in the observed spectrum. The breakdown of the selection rules can be accounted for qualitatively in terms of some simple perturbations not included in the original model.

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### Experimental Data

The fluorescence spectra of  $\text{GdAlO}_3:0.002 \text{ Cr}$  between 2 °K and 77 °K are shown in Figs. 1 and 2. All the data was obtained with the sample immersed in the cryogenic liquids in order to insure good thermal contact. The spectral bandwidth of the instrument was typically  $2\text{-}3 \text{ cm}^{-1}$ .

The bands shown in Fig. 1 around 735 nm have been identified as being due to  $\text{Cr}^{3+}$  pairs because of the quadratic dependence of their intensity on chromium concentration. The intensity of the overlapping bands between 723 and 730 nm vary linearly with chromium concentration and are believed to arise from the  ${}^2\text{E} - {}^4\text{A}_2$  transitions of isolated  $\text{Cr}^{3+}$  ions.

Notice in Fig. 1 that the emission spectrum at 77 °K consists of five clearly defined bands. When the temperature is reduced to that of boiling helium, the band on the high energy side disappears. The band with the greatest peak height narrows considerably and the peak to peak separations of the bands decreases slightly as the temperature decreases.

In Fig. 2 we see that the intensity of the band on the low energy side of the spectrum decreases, the bands continue to narrow and the peak to peak separations continue to decrease as the temperature is reduced from 4.4 to 2.15 °K. It is interesting to note that the relative heights of the two largest peaks are becoming more nearly the same as the temperature is lowered.

In Fig. 3 are shown the absorption spectrum at 2.2 °K corresponding to the  ${}^4\text{A}_2 \rightarrow {}^2\text{E}$  transitions as well as the fluorescence spectrum at that

temperature. Observe that the two curves overlap by more than 15 kT, many times the amount expected from the simple model, viz., kT. Furthermore, in the absorption spectrum, the low energy band is much more intense than the high energy band.

Measurements have been made of the fluorescence lifetime as a function of temperature at a number of wavelengths across the bands. It was observed that the lifetime is the same throughout, increasing with temperature between 2 °K and 77 °K and decreasing toward room temperature. The measured values at 2.2°K, 4.2°K, 77°K and 300 °K are respectively 9, 15, 18 and 13 milliseconds.

#### Theoretical Model

The structure<sup>3</sup> of  $\text{GdAlO}_3$  is orthorhombic but it has an almost cubic perovskite sub-structure with two equal sides of length 3.731 Å, the third of length 3.724 Å and a corner angle of 90.6°. The exact ion positions have not yet been obtained to our knowledge, although in the isostructural compound,  $\text{GdFeO}_3$ , which is somewhat more distorted from the cubic perovskite, the positions of the ions have been reported.<sup>4</sup> For similar ion positions in  $\text{GdAlO}_3$ , neither all the n.n.  $\text{Gd}^{3+}$  nor all the n.n.  $\text{O}^{2-}$  are equidistant from the  $\text{Al}^{3+}$  site so that symmetry allows four different exchange interaction strengths between the  $\text{Cr}^{3+}$  ions (substituted for  $\text{Al}^{3+}$ ) and the eight surrounding  $\text{Gd}^{3+}$  ions.

In attempting to understand the experimental results, we chose what we think is the simplest model consistent with the general features

of the chromium site. In this model we have assumed a cubic environment about each chromium ion and therefore the interaction with each of the eight nearest neighbor gadolinium ions is the same. Using an isotropic exchange interaction, the Hamiltonian is given by

$$H = -J \underline{S}_{Cr} \cdot \underline{S} \quad (1)$$

where  $\underline{S}_{Cr}$  denotes the spin of the chromium ion and  $\underline{S}$  denotes the total spin of the gadolinium environment and is given by

$$\underline{S} = \sum_i \underline{S}_i$$

The subscript  $i$  runs over the eight nearest neighbor gadolinium ions.

In this model, the chromium spin is coupled to the total spin  $S$  of the eight gadolinium ions. When the chromium ion is in the  $^4A_2$  state, its spin is  $3/2$ . The states that can be formed then have total angular moments given by  $|S| = |S + \frac{3}{2}|, |S + \frac{1}{2}|, |S - \frac{1}{2}|, \text{ and } |S - \frac{3}{2}|$ .

The interaction Hamiltonian is diagonal in  $S, S_z, S$  and  $S_{Cr}$ . The expectation value of equation (1) for states defined by the quantum numbers  $S, S_z, S, S_{Cr}$  are given by

$$\begin{aligned} & -J \langle S, S_z, S, S_{Cr} | \underline{S} \cdot \underline{S}_{Cr} | S, S_z, S, S_{Cr} \rangle \\ & = -\frac{J}{2} \{ S(S+1) - S(S+1) - S_{Cr}(S_{Cr}+1) \} \end{aligned} \quad (2)$$

independent of  $\mathcal{J}_z$ . The degeneracy of these energy levels is  $(2\mathcal{J} + 1)N_s$  where  $N_s$  is the total number of ways of forming a state of total spin  $S$  from the eight gadolinium ions, and  $(2\mathcal{J} + 1)$  is the azimuthal degeneracy of an angular momentum state  $\mathcal{J}$ . The problem of determining the quantities  $N_s$  has been discussed by Van Vleck.<sup>5</sup> However, his method was thought to be a little too cumbersome for eight ions each with spin  $7/2$  and therefore a different approach was taken. By adding two  $S_1 = 7/2$  spins together we form a set of resultants ranging in total spin from 0 to 7. We can then couple each of these to an identical set formed from a second pair to form a set of resultants with total spin ranging from 0 to 14. This set of four spins is then coupled to the remaining four to form the final set ranging in total spin from 0 to 28. The bookkeeping is relatively simple and when completed one finds the set of numbers shown in Table I

TABLE I

Total Number of Vectors of Length  $S$  Formed by Adding Together Eight Vectors of Length  $7/2$

$S$	$N_s$	$S$	$N_s$	$S$	$N_s$	$S$	$N_s$
0	11,096						
1	32,592	8	87,596	15	23,436	22	924
2	52,080	9	80,444	16	16,884	23	462
3	68,453	10	71,316	17	11,704	24	210
4	80,899	11	61,103	18	7,784	25	84
5	88,956	12	50,617	19	4,949	26	28
6	92,532	13	40,536	20	2,995	27	7
7	91,890	14	31,368	21	1,716	28	1

The degeneracy,  $(2\mathcal{L} + 1)N_g$ , of each of the states characterized by  $\mathcal{L}$ ,  $S$ , and  $S_{Cr}$ , with  $S_{Cr} = 3/2$ , is plotted in Fig. 4 as a function of its energy, as given by equation (2). The energy scale is in units of  $-J$  where  $J$  is the value of the exchange coupling constant. The broad band on the left of the figure corresponds to the band of states that have angular moments  $|S - 3/2|$ , the broad band on the right to those that have  $|S + 3/2|$ , while the dark narrow bands correspond to the  $|S - 1/2|$  and  $|S + 1/2|$  states respectively.

In order to relate this calculation to the experimental results, the state degeneracies were averaged over a small number of energy levels to form a "density of states". This curve was then compared to the shape of the fluorescence spectrum at 4.2 OK, adjusting the sign and magnitude of  $J$  to obtain a fit. The resulting curve for  $J = 2.1 \text{ cm}^{-1}$  is shown in Fig. 5 along with the emission spectrum at 4.2 OK. With this value of  $J$ , the energy of the transition to the  $S = 0$  states occurs at  $E_0 = 13,762 \text{ cm}^{-1}$ .

The agreement between the theoretical density-of-states curve and the fluorescence spectrum is somewhat disturbing since it implies that transitions are allowed from the upper level to every energy level of the ground state manifold which we have just considered. We will return to this point in a moment. First, let us determine the energy levels that exist when the chromium ion is in the  $^2E$  level.

The numbers of gadolinium states are the same as before and are given in Table I. Since, in the cubic field, the matrix elements of the spin orbit coupling vanish within manifold the  $^2E$  states, the spin and orbital

parts of the wave functions are free to orient themselves independently. This means that we can treat the state as if it were orbitally non-degenerate as far as the exchange interaction is concerned. The degeneracy will simply multiply the number of states by a factor of 2. The eigenvalues of the exchange interaction are given by equation (2) with  $S_{Cr} = 1/2$ . There are now two bands, one corresponding to the  $|S + 1/2|$  states the other to the  $|S - 1/2|$  states. The exchange parameter in the excited state may be different from that in the ground state. From the observed absorption spectrum shown in Fig. 3, the separation between the peaks of the two bands provides a value  $J' = 3.2 \text{ cm}^{-1}$ . The sign is again chosen by matching the relative peak heights of the calculated curve with the absorption data. In Fig. 6 we show the distribution of energy levels for both states of the  $Cr^{3+}$  ion for positive J.

It is evident that the simple model has features that relate to both the absorption and emission spectra. For instance, as the temperature is raised to 77 °K an additional band appears on the short wavelength side. The separation of the peak of this band from the peak of the nearest band to it is roughly equal to the separation between the peaks in the absorption spectrum. It seems reasonable to assume that this extra band arises from transitions between the  $S - 1/2$  excited band to the  $S + 3/2$  ground state band. The other transitions from the  $S - 1/2$  excited band are superimposed on the transitions from the  $S + 1/2$  band and presumably contribute to the excess width of the main peak at 77 °K. There is an indication of a bump on the short wavelength side of the highest peak which is just where the  $S - 1/2$  to  $S - 1/2$  transitions would peak.

### Breakdown of Selection Rules

We encounter difficulties as soon as we inquire into the selection rules for optical transitions between the upper and the lower bands. It seems entirely reasonable that the Cr-Gd system should be in thermal equilibrium with the lattice. Even in the absence of any exchange coupling between the gadolinium ions, the dipole-dipole interaction can relax the Cr-Gd system. If equilibrium exists, the fluorescence at 2.2 °K occurs from the lowest levels of the upper manifold in Fig. 6. Our observation of a uniform fluorescence decay rate throughout the bands supports this argument. We are confident that the system was in the thermal equilibrium before the absorption measurements.

The following considerations determine the selection rules for our simple model. Because the transitions involve the coupling of a  $\text{Cr}^{3+}$  moment to the electromagnetic field, the total spin,  $S$ , of the gadolinium ions is conserved. In the limit of low temperatures, we should then see four sharp lines in fluorescence, the long wavelength line noticeably weaker than the other three because of the selection rules on the chromium transitions. For example, it is known that for  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$ <sup>6</sup> there is a selection rule on the chromium transitions, namely,

$$\begin{aligned} |^2E, +\frac{1}{2}\rangle &\leftrightarrow |^4A_2, -\frac{3}{2}\rangle = 0 \quad , \\ |^2E, -\frac{1}{2}\rangle &\leftrightarrow |^4A_2, +\frac{3}{2}\rangle = 0 \quad . \end{aligned} \tag{3}$$

It is straightforward though somewhat arduous to show that the matrix



elements for transitions between the  $S + 1/2$  band in the excited state and the  $S - 3/2$  band in the ground state are much smaller than the transitions to the other three bands because of the selection rules given by equation (3) and the requirement that matrix elements are non-vanishing only between parts of wave functions that have the same gadolinium components.

Because of the same selection rules, the absorption spectrum should consist of two sharp lines at  $T = 0$ . The longer wavelength absorption line would correspond to the  $|S + 3/2|$  to  $|S + 1/2|$  transition (with  $S = 28$ ) while the higher energy line would correspond to the  $|S + 3/2|$  to  $|S - 1/2|$  transition. Again the  $|S + 3/2|$  to  $|S - 1/2|$  matrix elements are smaller than those to the  $|S + 1/2|$  states because of equation (3) and the requirement on the gadolinium spins.

Since sharp lines are not observed in the spectrum there is either a breakdown in the selection rules obtained from the simple model or there is large inhomogeneous broadening of the levels. The shape shown in Fig. 3 of the emission spectrum at 2.2 °K suggests that transitions from a small number of levels at the bottom of the excited manifold are allowed to a continuous distribution of states of the ground manifold. A similar statement applies to the absorption spectrum at 2.2 °K.

On reducing the temperature from 4.2 °K to 2.2 °K we see in Fig. 2 that the  $S + 1/2$  to  $S - 3/2$  band in emission disappears or at least decreases in intensity relative to the rest of the bands. We can account for the behavior just described if we assume that what we have been calling the  $|S - 3/2|$ ,  $|S - 1/2|$ , etc. bands are bands that correspond

to the  $-3/2$ ,  $-1/2$ , etc. projections of the chromium ion on its environment but the environmental spin  $S$  is not a good quantum number. Such a situation would exist if, instead of the isotropic exchange interaction that we chose to describe the system, we had used an Ising model with

$$H' = -J S_{Cr_z} S_z,$$

where

$$S_z = \sum_1 S_{z1},$$

the subscript 1 running over the eight nearest neighbor gadolinium ions. This interaction would again result in a density of states that consists of four parts. However, it is not difficult to see that the  $S_{Cr_z} = +3/2$  and  $S_{Cr_z} = -3/2$  parts would be mirror images of each other and that the two together would form one band with its peak at  $S_z = 0$ . The  $S_{Cr_z} = +1/2$  and  $S_{Cr_z} = -1/2$  parts would also be mirror images peaking again at  $S_z = 0$ . The width of the  $\pm 1/2$  band would be  $1/3$  that of the  $\pm 3/2$  band as they are in the isotropic exchange model. Therefore, the  $\pm 1/2$  band would sit on top of the  $\pm 3/2$  band. This new model would predict zero transition probability between the  $+1/2$  excited states and the  $-3/2$  ground states, and between the  $+3/2$  ground states and  $-1/2$  excited states. It is interesting that at the lowest temperatures measured, the emission spectrum does appear to be approaching this model insofar as the  $+1/2$  to  $-3/2$  band has disappeared and the relative intensities of the transitions to the  $+1/2$  and  $-1/2$  states from the  $+1/2$  excited states are becoming equal.

There are a number of things obviously wrong with our original model. The most obvious are:

- a) we have neglected Gd-Gd interactions;
- b) we have assumed the coupling of the  $\text{Cr}^{3+}$  ion to each nearby  $\text{Gd}^{3+}$  ion to be the same and described by an isotropic exchange interaction;
- c) we have assumed cubic field about the  $\text{Cr}^{3+}$  ions.

Lifting either a) or b) will remove the selection rule on the Gd spins during the transitions. This is necessary in order to account for the broad bands in the spectra if we assume negligible inhomogeneous broadening. The distortions of the  $\text{Cr}^{3+}$  environment from cubic symmetry are not purely trigonal and therefore there is a crystalline field splitting of the  $^2\text{E}$  level. It is felt, however, that if the crystalline field splitting were comparable with the splitting due to an exchange coupling with  $J = 3 \text{ cm}^{-1}$ , we would have expected two sets of two bands in absorption, one set shifted from the other by the amount corresponding to the crystalline field splitting. This does not appear to be the case.

It has been pointed out to us by Burns<sup>7</sup> that  $\text{GdAlO}_3$  orders antiferromagnetically at a temperature near  $4^\circ\text{K}$ . This would require a Gd-Gd exchange constant of  $J''$  of about  $0.1 \text{ cm}^{-1}$ .<sup>8</sup> Such an ordering would tend to narrow the  $S + 3/2$  and  $S + 1/2$  bands and broaden the  $S - 1/2$  and  $S - 3/2$  in the ground state because the large angular momentum states of the gadolinium system would be raised while small angular momentum states would be lowered. These changes are in the right direction to bring the calculated density of states curve of Fig. 5 in closer agreement with the  $4^\circ\text{K}$  emission spectrum.

-

We have not discussed the overlap between the absorption and the emission spectrum shown in Fig. 3 and the temperature dependence of the radiative lifetimes. The lifetimes require more detailed knowledge of the Cr-Gd wave functions which we do not have at the present time. The overlap of the absorption and emission bands may be an experimental anomaly arising from errors in determining the base line. If it turns out to be a real effect, it may be caused by a variation of 10% in the Cr-Gd coupling at different chromium sites. However, we feel at the present time, that we may not be able to fit the overlap line shape with a model based on inhomogeneous broadening.

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### Figure Captions

- Fig. 1 Fluorescence spectra of  $\text{GdAl}_{.998}\text{Cr}_{.002}\text{O}_3$  at 77 and 4.2 °K.
- Fig. 2 Fluorescence spectra of  $\text{GdAl}_{.998}\text{Cr}_{.002}\text{O}_3$  at temperature between 2.15 and 4.40 °K.
- Fig. 3 Absorption and fluorescence spectra of  $\text{GdAl}_{.998}\text{Cr}_{.002}\text{O}_3$  at 2.2 °K.
- Fig. 4 Degeneracy vs. energy for an interaction  $-J \underline{S}_{\text{Cr}} \cdot \underline{S}$  with  $\underline{S}_{\text{Cr}} = 3/2$  and  $0 \leq S \leq 28$ , where  $S$  is the total angular momenta of the Gd environment.
- Fig. 5 A comparison of the fluorescence intensity of  $\text{GdAlO}_3:\text{Cr}$  at 4.2 °K with the theoretical density of states with  $\underline{S}_{\text{Cr}} = 3/2$ . The theoretical bandwidth signifies the range of energy states whose degeneracies were averaged to obtain a density of states.
- Fig. 6 The number of states that are degenerate vs. energy for both the  $^2\text{E}$  and  $^4\text{A}_2$  states of  $\text{Cr}^{3+}$  interacting ferromagnetically with the  $^8\text{S}_{7/2}$  states of each of the eight surrounding  $\text{Gd}^{3+}$  ions. The figure have been drawn using a value of 1.5 for the ratio of exchange parameters for the  $^2\text{E}$  and  $^4\text{A}_2$  states of  $\text{Cr}^{3+}$  as indicated by the experimental results. The labels on the right designate the total angular momenta of the coupled Cr-Gd system.

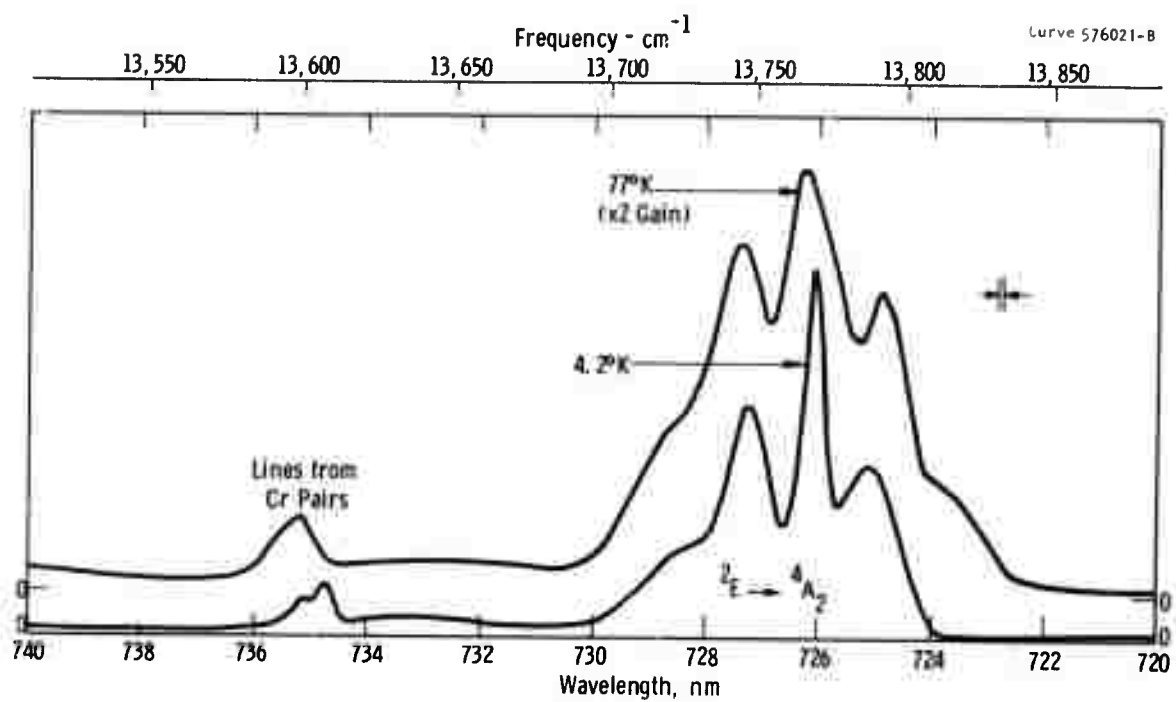


Fig. 1

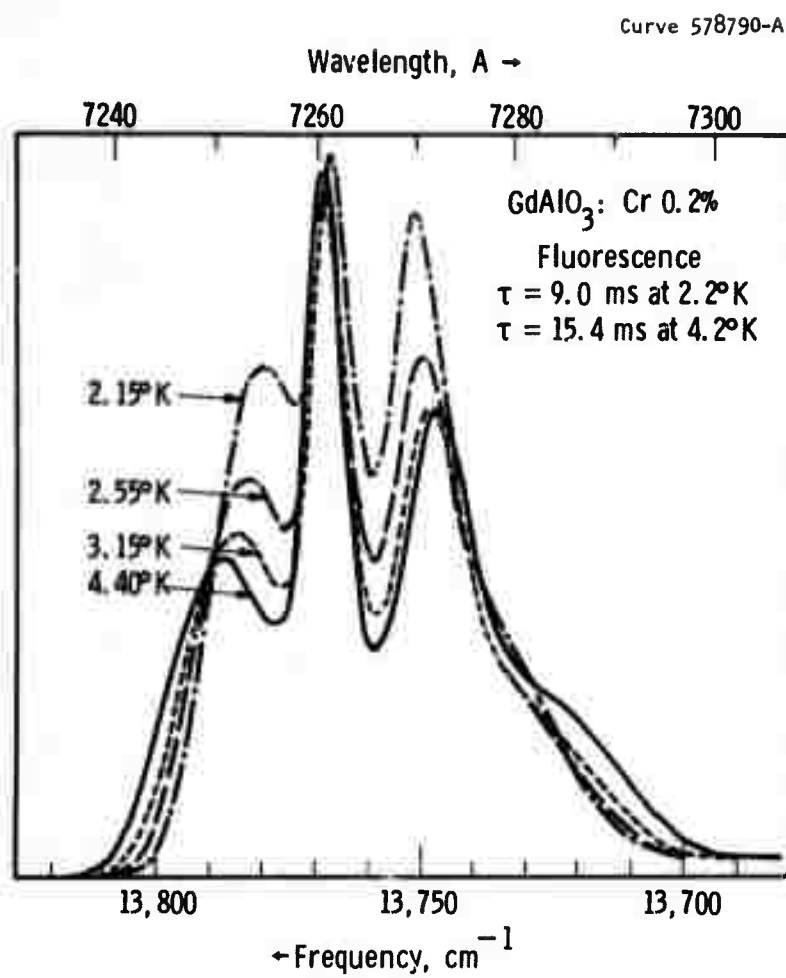


Fig. 2



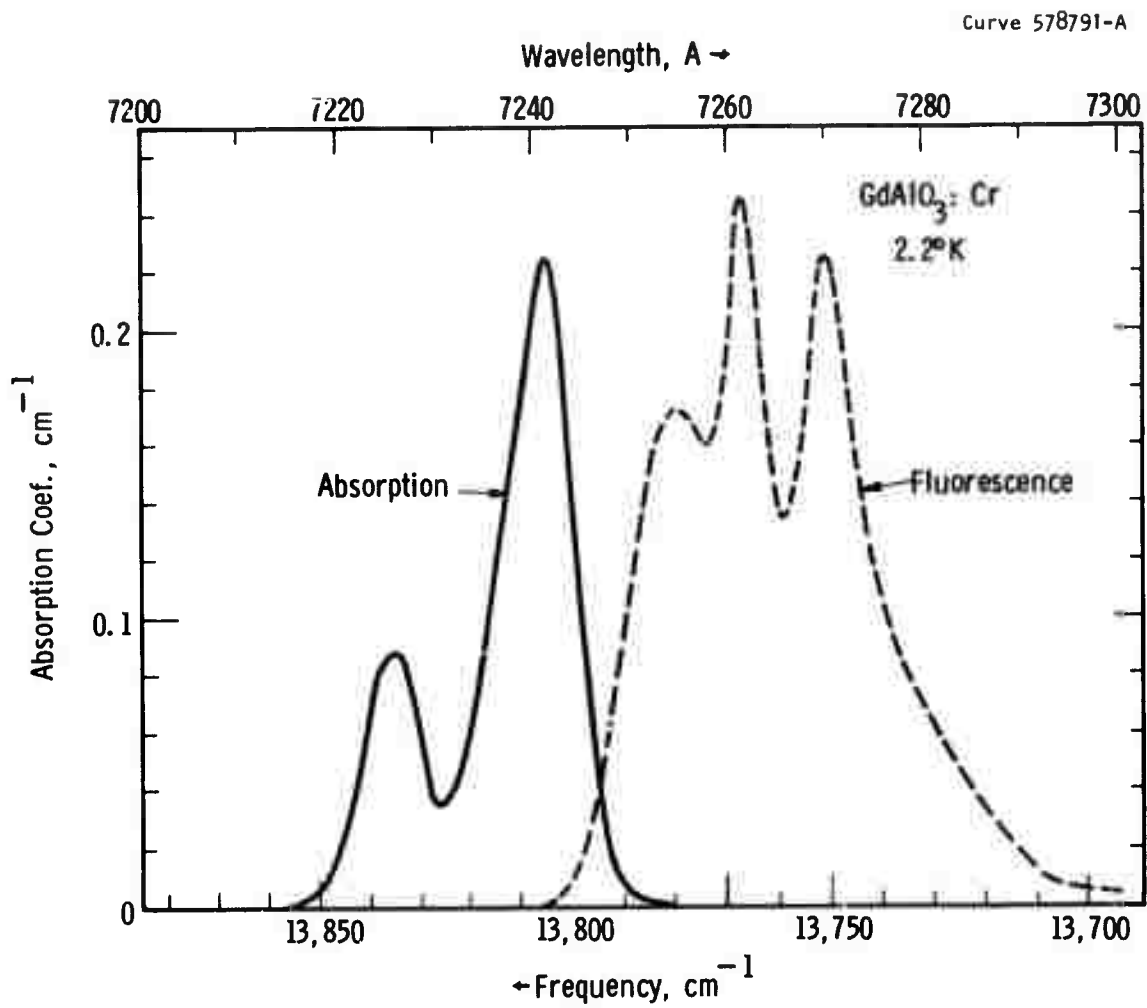


Fig. 3

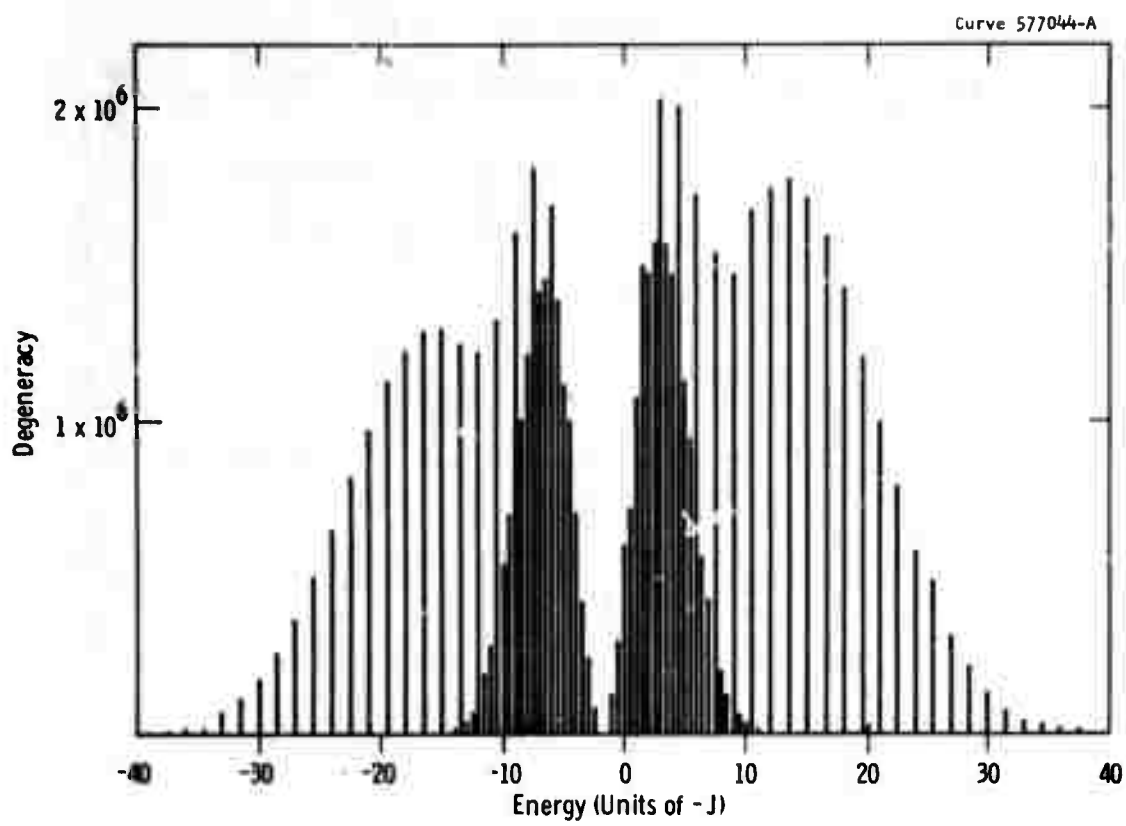


Fig. 4

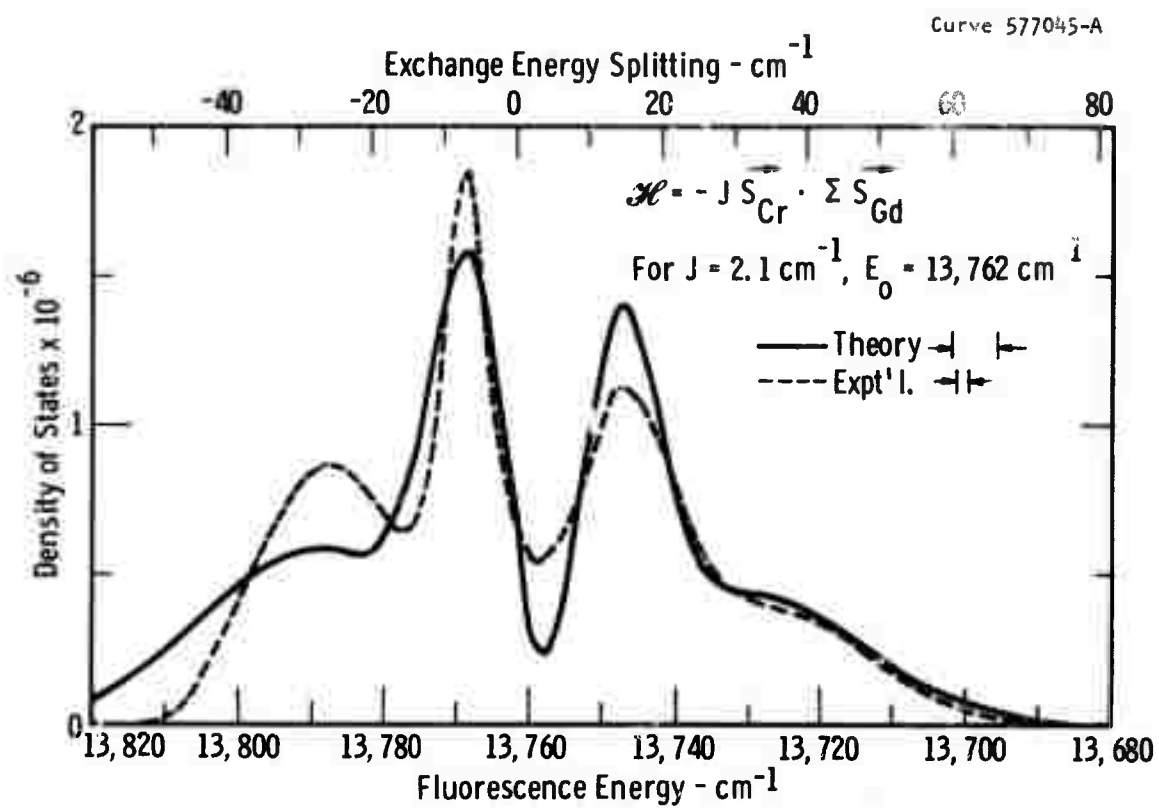


Fig. 5

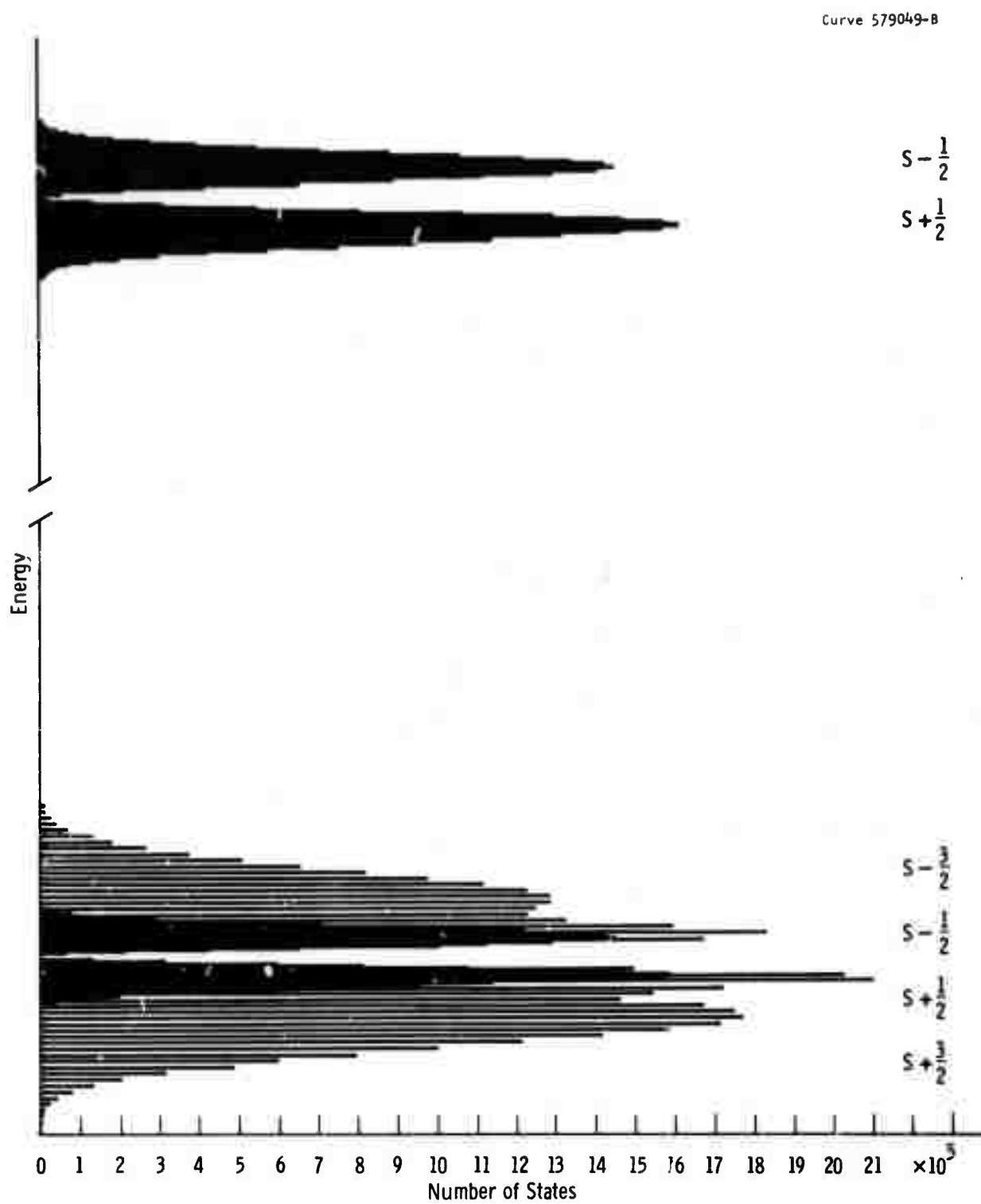


Fig. 6

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